

CATALYST REGENERATION

SUMMARY

The continuous regeneration of FCC catalyst has been the subject of many developments in the past, resulting in the construction of smaller regenerators, with lower catalyst inventories, operating at higher temperatures. The reduction in catalyst holdup permits faster catalyst replacement through regular catalyst addition and withdrawal. The biggest development in catalyst regeneration was the use of CO combustion promoter. This allowed better control of the regenerator temperature and improved flexibility of operation in terms of air consumption and flue gas composition.

CONTENTS:

1. Introduction
2. Coke burning
3. Combustion promoter
4. Partial CO combustion
5. Complete CO combustion
6. Monitoring the regeneration
7. Novel non-platinum based CO combustion

1. INTRODUCTION

Catalyst leaving the FCC reactor usually contains around 1 wt% coke, with a carbon to hydrogen atom ratio of near unity. The main objectives of regeneration are to burn off the coke from the catalyst to restore its activity, and to maintain the heat balance in the unit. The heat generated by the major reactions is shown in table 1. Strictly speaking, the combustion of sulfur and nitrogen compounds in the coke also generates heat. Their contribution is minor and can be neglected.

Table 1: Heat effects of coke burning

Reaction	Product	Heat release
$C + \frac{1}{2} O_2$	$\rightarrow CO$	2200 cal/g C
$CO + \frac{1}{2} O_2$	$\rightarrow CO_2$	5630 cal/g C
$C + O_2$	$\rightarrow CO_2$	7830 cal/g C
$2H + \frac{1}{2} O_2$	$\rightarrow H_2O$	28700 cal/g H

The total heat generated depends on the hydrogen content of the coke, the level of CO combustion, and the coke yield. Depending on stripper efficiency and the strippability of the catalyst, the hydrogen content of coke normally varies from 6 to 8

wt%. The effect of CO combustion at 7 wt% hydrogen in coke is indicated in figure 1.

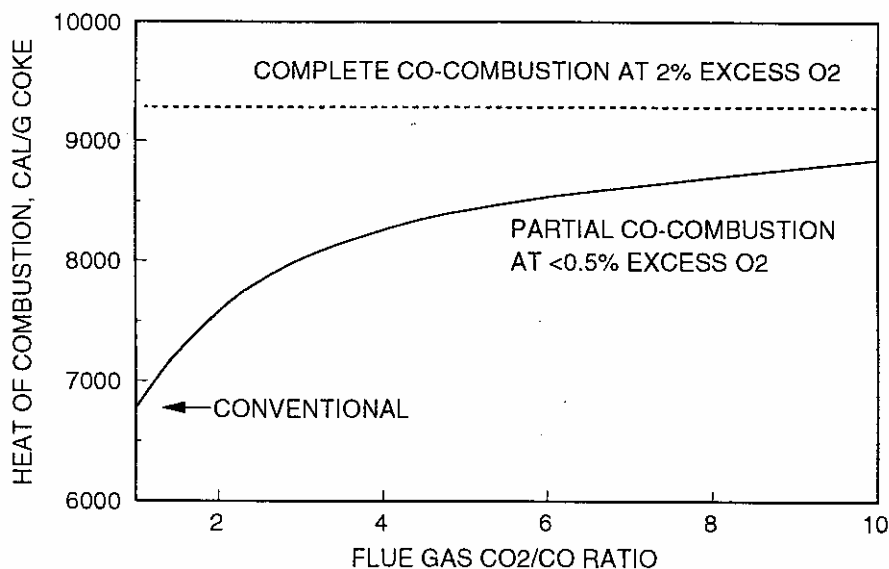


Figure 1: Effect of CO combustion extent on the heat of combustion

In practice, the coke yield in FCC is maintained at a relatively constant level, frequently utilizing the full capacity of the air blower. However, coke on spent catalyst from the reactor can vary substantially, depending on the feed quality, catalyst activity and its coke-selectivity. These variables can force changes in regenerator conditions such as temperature or amount of carbon remaining on the regenerated catalyst (CRC). This had been difficult to control in what is termed conventional combustion (CO₂/CO in flue gas near a volume ratio of 1).

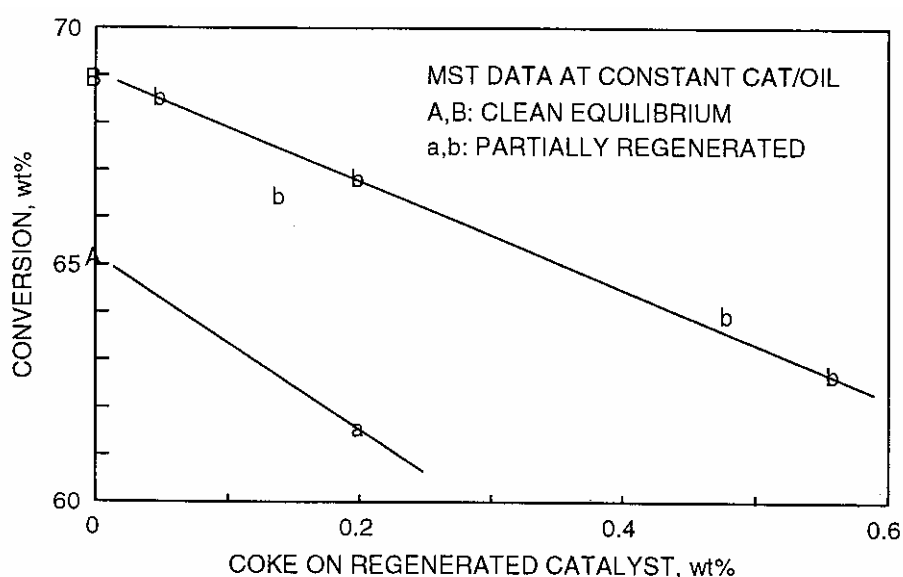
2. COKE BURNING

Initially, regeneration occurred in conventional combustion, with dense bed temperatures well below 700 °C (1300 °F), more typically around 650 °C (1200 °F). Coke burned roughly equally into CO and CO₂ in the dense phase, with some additional CO combustion occurring in the dilute phase, called “afterburning”. Typical CO₂/CO ratio in the flue gas would be around unity with an excess oxygen less than 0.5 vol%(1). A CO boiler is normally then employed to reduce CO to acceptable levels and recover the remaining energy from the flue gas. Combustion in the CO boiler can be carefully controlled; with proper hardware and conditions NO_x emissions can be minimized to well below 100 ppm in a modern boiler.

Under conventional combustion conditions, increasing the air rate causes an increase in afterburning, while a reduction results in residual coke on regenerated catalyst (CRC) increasing, lowering the catalyst activity sent to the reactor. Attempting to maintain reactor temperature constant under the latter conditions will push up cat-to-oil ratio (C/O), decrease regenerator temperature, and lead to yet more residual coke, and so on, until the system may become inoperable. This has been called the “snowball” effect, and is also known as “behind in burning”. It should be noted that this results from trying to maintain reactor temperature by increasing C/O – had

reactor temperature been permitted to fall, and C/O held constant, the system would have equilibrated at the higher CRC and a lower reactor temperature. Hence constant catalyst circulation units, such as an Esso Model IV, which use pressure balance rather than slide valves to set cat circulation, have operated at high CRC's – even at 0.5 to 1 wt%, though this is not recommended.

The effect of residual coke on the catalyst activity is illustrated in figure 2. The activity increases when CRC is reduced, the extent of which depends on the catalyst type and activity level (1 to 2 wt% conversion per 0.1 wt% coke). Older FCC units with carbon steel cyclones in the regenerator are often limited by metallurgy to about 680 °C (1260 °F), while newer units with stainless steel metallurgy permit operation up to 760 °C (1400 °F) or somewhat higher. With properly designed (and operating) air distributors and dense bed temperatures of 700 °C⁺ (1290 °F⁺), low levels of CRC are easily obtained (so long as the air blower limit is not exceeded. Higher regenerator temperatures assist in maximizing use of air to burn coke, rather than CO



in the flue gas.

Figure 2: Effect of CRC on activity for two different catalysts (2)

The effects of CRC on overall catalytic activity in the unit, and on catalytic selectivity, are more difficult to quantify due to concurrent changes in catalyst circulation. Catalysts with higher CRC make less gasoline, but also less coke, so that in a heat-balanced system at constant coke yield the combined effects are less clear. They also depend on the type of catalyst and how the residual coke is distributed over its active surface area (figure 3).

Moderate levels of residual coke on catalyst may even have a positive effect on the yield structure in commercial operation (2). This depends on unit conditions and catalyst properties, such as zeolite content. Laboratory studies (and commercial experience) have shown little detrimental effect on conversion or selectivity for valuable products at CRC up to about 0.35 – 0.4%, as long as catalyst circulation is not limiting and C/O can increase to compensate for lower individual catalyst activity.

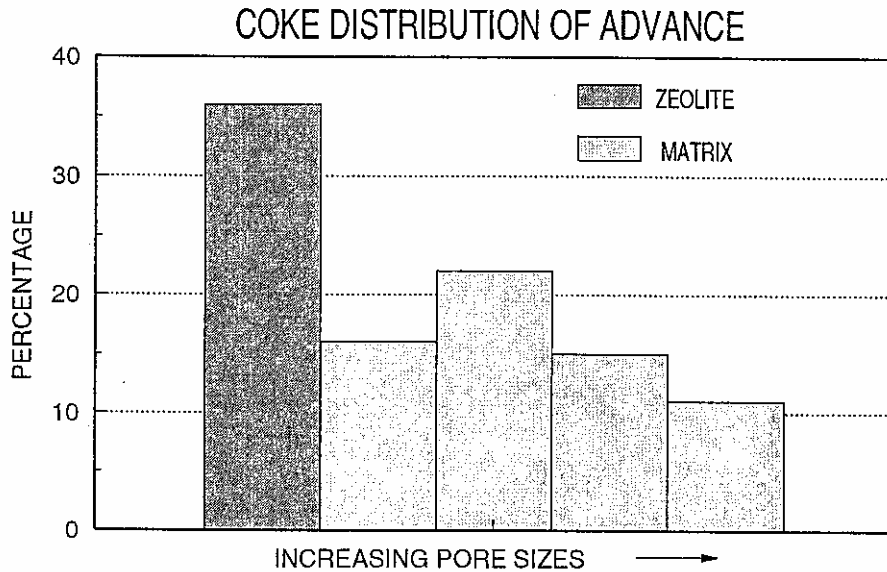


Figure 3: Typical carbon profile of FCC catalyst (2)

The lowest level of CRC is achieved with complete CO combustion and excess oxygen in the flue gas. Complete CO combustion without use of promoter is possible, but can require high excess oxygen (> 3%) and regenerator dense bed temperature above 700 °C. However, such operations can lead to considerable afterburning, which is a waste of air blower capacity and limits regenerator bed maximum temperature (maximum bed temperature = maximum cyclone / downstream flue gas temperature – amount of afterburn).

3. COMBUSTION PROMOTER

The use of small amounts of noble metals, mainly platinum (Pt), to promote CO combustion in the regenerator was discovered by Mobil Oil Corporation in the seventies. Use of ppm levels on FCC catalyst proved very effective in reducing or even eliminating afterburn. The required traces of noble metal can be put on the fresh catalyst (factory promoted, called INSITUPRO by Albemarle) or on a separate powder mixed in with the catalyst or injected separately into the FCC unit (called Combustion Additive).

Combustion additives contain several hundred ppm noble metal, i.e. Pt. Ideally 1 to 2 kg additive per ton of fresh catalyst is sufficient to control CRC, reduce afterburn, and avoid excess NO_x emissions (high excess oxygen and Pt generate excess NO_x). For a proper regeneration, besides effective air distribution, the important factors are the level of Pt on inventory and mixing of the additive with the circulating catalyst. Especially for large inventory units, it is important to ensure good distribution of the promoter. This is best achieved with factory promoted catalyst, which requires less Pt in inventory for the same amount of afterburn as combustion additives and hence generates less NO_x. Combustion additives are more flexible in responding to varying regenerator conditions.

Combustion additive can move a unit into promoted CO combustion by addition through the fresh catalyst makeup line, typically using a small additive hopper (blow pot). Additions are made at intervals (e.g. every 15 minutes) until 1 kg of additive per ton of catalyst inventory has been achieved, typically in a couple hours. Daily consumption of additive varies with catalyst addition rates and feed characteristics. After the first batch of promoter has been added to the regenerator, an immediate effect is seen. In partial CO combustion, the dense phase temperature will rise and CO boiler steam make drop (supplemental fuel can be increased to maintain boiler steam production). At this point no adjustment in air rate is needed, but catalyst color should be checked frequently (e.g., every 30 minutes). In partial burn with promoter, the regenerator dense bed temperature depends on the air rate, the afterburn on activity of promoter.

As promoter concentration is increased, the dilute phase temperature continues to drop, to the level of the dense bed. In complete combustion with sufficient additive, the flue gas temperature may even stabilize at a lower level than the bed. This can result from heat losses in the dilute phase that are no longer compensated by afterburn. Occasionally, with poor air distribution or damaged air grids, not all temperatures in the dilute phase drop equally, and “hot cyclones” can occur where individual cyclones display afterburn even though others do not. This has a negative impact on catalyst deactivation, because catalyst circulation through the cyclones (especially the first stage) is significant.

In figure 4, an example of promoter usage is shown. In this case the objective was to improve combustion and reduce CRC, by increasing regenerator bed temperatures with partial CO combustion. A small level of afterburning was permitted, to minimize consumption of the additive when steady state was attained.

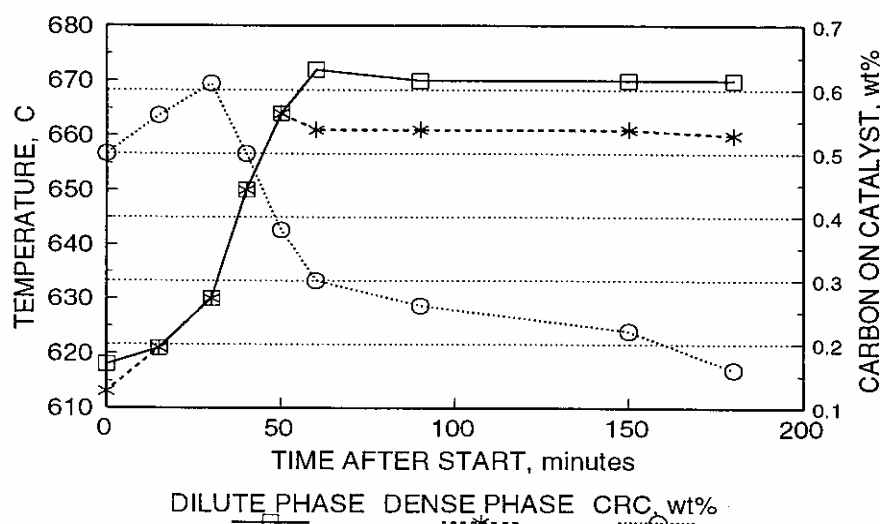
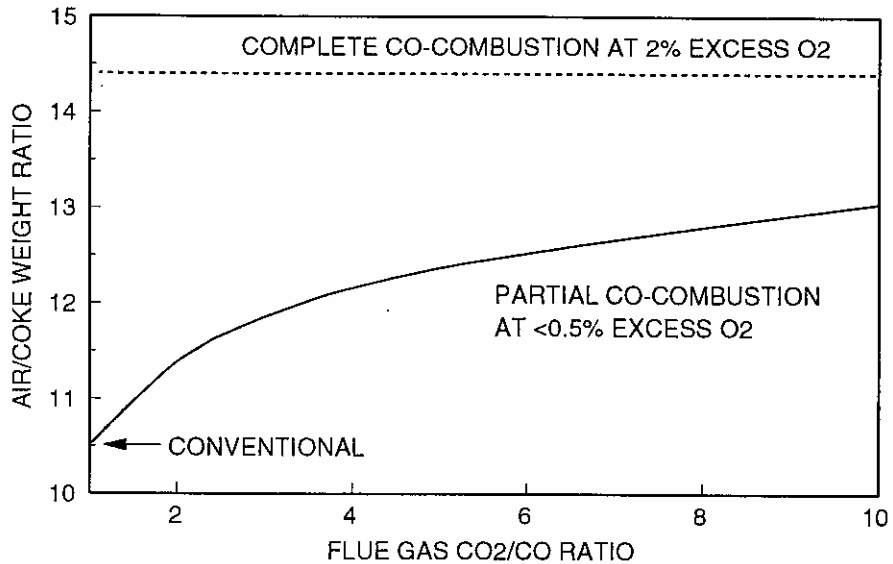


Figure 4: Effect of promoter on CRC (startup example)

4. PARTIAL CO COMBUSTION

Increased CO combustion not only results in a higher heat of combustion (figure 1), but also in higher consumption of air per ton of coke (figure 5). However, on a per ton of feed basis, the air rate drops with increased CO combustion, until the excess oxygen in the flue gas builds up (figure 6). The maximum feed capacity in partial combustion can be observed at about 1 vol% CO in the flue gas ($CO_2/CO = 16-17$) at



constant air rate.

Figure 5: Effect of CO combustion on air/coke ratio

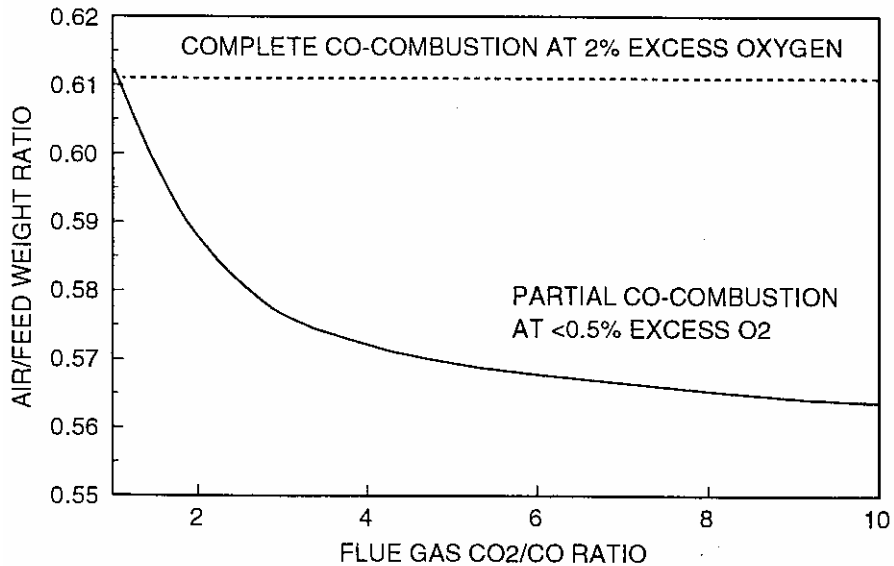


Figure 6: Effect of CO combustion on air requirement

5. COMPLETE CO COMBUSTION

Complete CO combustion requires more air to burn the same amount of coke due to the excess oxygen in the flue gas. The CO must be eliminated from the dilute phase to control afterburning and avoid hot cyclones. Commercial data from various units running in complete CO combustion show clear evidence of promoter concentration on amount of afterburning (table 2).

Table 2: Effect of CO promoter on afterburning

Unit [*]	Pt in unit, ppm	Regenerator Bed Temperature, °C	Afterburning ΔT, °C
A	3	720	0
B	3	750	3
C	3	718	4
D	1.5	730	10
E	1	720	10
F	0	715	35
G	0	695	35

Units A – D use factory promoted catalyst, unit E uses separate additive

The dense bed temperature moves up and down with the feed quality and catalyst activity, i.e., delta coke on catalyst. Excess oxygen levels help to deactivate the nickel deposited on catalyst, but accelerate vanadium attack and deactivation of the catalyst.

As feed becomes heavier, with increased amounts of coke precursors, delta coke on catalyst increases and the maximum design temperature of the regenerator vessel and/or internals will eventually be reached. As mentioned in FCC Manual 5.1, excess oxygen can be employed to remove some of the heat with the flue gas, but unlike partial combustion (where wide swings in CO₂/CO offer flexibility in temperature control) this will only reduce temperature a small amount and reduces coke-burning capacity. The higher regenerator temperature also increases catalyst deactivation, aggravated by metals and steam.

The FCC regenerator can be regarded as an inferno for the catalyst (3). Some irreversible transformations take place in the catalyst at high temperatures, especially in the presence of steam, so adding steam or water to reduce temperatures is not recommended. Steam (or water) should be added to the reactor/stripper side of the unit if possible, where residence time and temperature of the catalyst are considerably lower than during regeneration. Eventually, installation of a catalyst cooler is recommended. This reduces bed temperature, and catalyst deactivation rate. However it will also require additional air capacity, to handle the increased coke yield, or increased feed preheat to compensate the cat cooler heat removal. The overall effect depends on the heat balance of the FCC.

The FCC operating flexibility can be improved by “oxygen enrichment”, either continuously or intermittently, particularly in combination with a cat cooler(4). This adapts the operation to heavier feedstocks, maintaining conversion or alternatively, increasing throughput capacity at constant feed quality. The injection of oxygen should be in the air line to the regenerator, to avoid local increases in catalyst temperature and additional catalyst deactivation. Oxygen enrichment to 26% concentrations has been routinely operated, with proper safety interlocks (5).

6. MONITORING THE REGENERATION

The quality of regeneration is monitored by visual inspection of a sample of the regenerated catalyst. Typically sampled once per day (or even once per week) during smooth operations, once per shift or more frequently during upsets or major changes, it should have a uniform light gray color (often referred to as “mouse gray”). The exact color is less important than its match to known samples of catalyst with acceptable levels of CRC, and that it is not getting darker over time (sign of insufficient air). A salt and pepper appearance is also unwanted, indicating poor air or catalyst (i.e., coked spent catalyst bypassing) distribution. Air distribution problems will also be apparent from increased cyclone inlet/outlet temperatures in a particular section of the regenerator (hot cyclones).

Regeneration can normally be improved by increasing catalyst bed level (inventory) or by increasing regenerator temperature (e.g., increasing catalyst makeup rate, activity). In complete combustion, increased air results in lower regenerator temperature (since there is no more CO to burn, the extra gas volume removes heat). In partial combustion of course, increased air will increase regenerator temperature.

By increasing the promoter activity, afterburn can be controlled, but at some point adding more promoter will have no effect. Overpromotion may even lead to local oxygen depletion, and will generate more NO_x. CO promotion performance of the unit’s circulating catalyst can be tested in the laboratory, but provides only relative combustion activity. In case of doubt, a quick check is made by adding a batch of new promoter to the regenerator and watching the response of the regenerator bed and flue gas temperatures.

7. NOVEL NON-PLATINUM BASED CO COMBUSTION

For more than 30 years, platinum-based combustion promoters have been utilized in FCC units to catalyze the oxidation of CO to CO₂. The better the dispersion of platinum, the more effective is the combustion of coke. When platinum-based CO combustion promoters are added, the oxidation of HCN, NH₃ and other reduced nitrogen intermediates to NO increases. In addition, the amount of gas phase reductants (such as CO) decreases, further reducing the presence of reductants to react with NO. In summary, the use of platinum-based CO combustion promoters leads to an increase in NO_x formation (Figure 7).

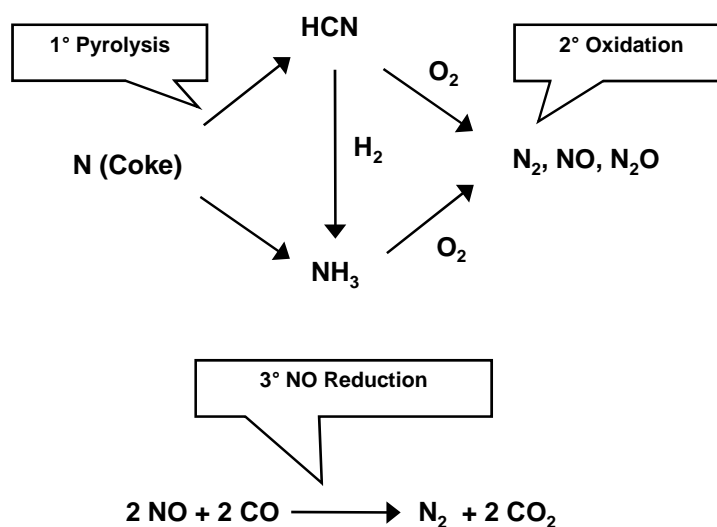


Figure 7: NO_x chemistry in an FCC unit

More recently new non-platinum CO combustion promoters have been developed. First generation non-platinum CO combustion promoters were susceptible to activity maintenance problems. A loss of metals dispersion occurred due to agglomeration, while pore collapse of the support gave rise to surface metal encapsulation. As a result, the effective half-life was shorter than conventional platinum-based promoters, leading to increased product usage.

Albemarle's ELIMINO_x, is a material that effectively controls CO emissions and afterburn without increasing NO_x emissions like conventional platinum-based additives.

ELIMINO_x features a support with improved hydrothermal stability together with higher metals loadings. It contains Albemarle's unique bimetallic design for efficient CO oxidation without concern for poisoning by sulfur-containing molecules.

Figure 8 confirms that ELIMINO_x effectively lowers the emission of NO_x compared to traditional platinum-based combustion promoter. This was obtained while at the same time smooth combustion operation was also maintained.

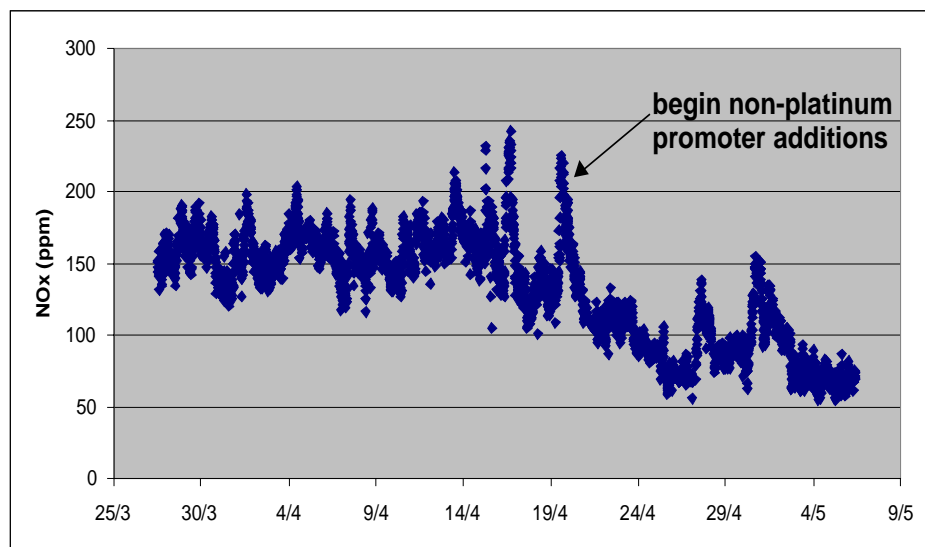


Figure 8: Reduced NO_x with ELIMINOx, a novel non-Pt based combustion promoter

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